

# Molecular Structures and Conformations: Experiment and Theory

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**ABSTRACT:** Theoretical calculations in combination with experimental gas phase structure research can be performed in two ways. The first is to support and improve experimental analyses by including additional data from theoretical calculations. This is to the advantage of the experiment. The second way is a comparison of geometric structures and conformational properties obtained with different theoretical methods with the experimental result. This comparison indicates which theoretical method or methods are suitable for a specific compound. This approach is to the advantage of the theory. © 1998 John Wiley & Sons, Inc. *J Comput Chem* **19**: 123–128, 1998

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## Introduction

About 25 years ago experimental and theoretical studies of molecular structures and conformational properties were done quite separately. Because theoretical methods have also become applicable for reasonably sized molecules, experimental investigators started to take advantage of these methods and included molecular mechanics (MM), semiempirical, and later *ab initio* and/or density functional (DFT) calculations in their experimental analyses. Today, because computer programs are very easy to use and sufficient computer capacity is generally available, most experi-

mental studies of gas phase structures by gas electron diffraction (GED), microwave (MW), or high-resolution infrared spectroscopy are combined with theoretical calculations. This combination of experimental and theoretical methods is to the advantage of both experiment and theory.

## Advantage for Experiments

In the case of GED studies, MOCED (Molecular Orbital Constrained Electron Diffraction) has been suggested by L. Schäfer for such a combination.<sup>1</sup> Some information from theoretical calculations that can support the analysis of experimental data is collected in Table I. If a molecule contains closely spaced interatomic distances of the same kind (e.g., similar C—C bonds or 1,3-nonbonded C···C dis-

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**TABLE I.**  
**Information from Theoretical Calculations Which Support an Experimental GED Analysis.**

Problem in GED analysis	Information from theoretical calculations
Closely spaced distances	Differences between distances of the same type
Location of hydrogen atoms	Respective parameters (e.g., HXH angle)
High correlations between geometric parameters and vibrational amplitudes	Vibrational amplitudes from force field
Several conformations	Conformational space (type of possible conformations); differences between geometric parameters of different conformers

tances, the mean value can be determined very accurately in a GED experiment, but not the individual values. If these differences are derived with a theoretical method, their inclusion in the experimental analysis allows for determination of reliable values for the individual bond lengths or angles. It is generally assumed that differences between such distances depend little on the method of calculation. A realistic estimate of the uncertainty for such differences is  $\pm 1$  pm. Due to the small scattering amplitude of hydrogen atoms the location of hydrogen atoms is often badly determined in a GED experiment. The corresponding parameters, such as H—X—H angles, can be taken from theoretical calculations. For many molecules, high correlations between geometric parameters and vibrational amplitudes cause large standard deviations for some parameters. The use of vibrational amplitudes that are calculated from theoretical force fields can increase the accuracy for geometric parameters considerably. In conformational analyses, theoretical information about the conformational space (i.e., about the type of possible conformations), which represent minima on the energy hypersurface, is of great help in experimental analyses. Furthermore, differences between corresponding bond lengths and bond angles in the various conformers that cannot be determined experimentally can be transferred from theoretical calculations. The inclusion of such additional information from theoretical methods in the experimental analyses leads to a great improvement of the results; that is, to a decrease in experimental uncertainties.

### Advantage for Theory

The second aspect of combining experimental and theoretical methods is a comparison of experi-

mental results and those obtained with different theoretical methods. Ideally, all theoretical results for bond lengths, bond angles or conformational properties agree with each other within a small range. In many cases, however, the results differ appreciably. The comparison with experimental data demonstrates which method or methods work properly and which do not for a specific molecule. This combination between experiment and theory is to the advantage of the theoretician. For the comparison between experimental and theoretical results we must consider systematic differences between the vibrationally averaged parameters from the experiment ( $r_g$ ) and the equilibrium value from theory ( $r_e$ ). For bond lengths,  $r_g$  values are about 0.4–0.9 pm longer than  $r_e$  values (1.4–1.8 pm for X—H bonds), and for bond angles the differences are assumed to be small. Vibrational effects can cause differences of  $10^\circ$  or more for dihedral angles. In conformational analyses we compare experimental  $\Delta G^0$  values with calculated relative energies,  $\Delta E$ . For reasonably rigid conformers and for equal statistical weights this difference is smaller than 0.2 kcal/mol. Furthermore, we cannot expect that theory reproduces experimental results perfectly (i.e., within the experimental uncertainties). We consider the agreement to be satisfactory if bond lengths are reproduced to within  $\pm 3$  pm, bond angles within  $\pm 3^\circ$ , dihedral angles within  $\pm 10^\circ$ , and energy differences within  $\pm 0.5$  kcal mol<sup>-1</sup>.

In this sense theoretical methods reproduce molecular structures of many molecules satisfactorily. Such compounds are a delight for the theoretician and a disappointment for the experimentalist. Obviously, it is disappointing to spend weeks or months on an experimental analysis to find out that a theoretician gets the same result in a few hours or overnight. Fortunately, there is a good number of molecules for which the application of

theoretical methods for predicting geometric structures or conformational properties is not a straightforward procedure. In 1978, H. F. Schaefer reported at the Austin Symposium on Gas Phase Structures about his obstinate, but unsuccessful, attempts to reproduce the experimental structure of FOOF and he ended his lecture by calling this molecule a "theoretician's nightmare." The experimental investigator however, loves such molecules. We will now present a few examples from our laboratory where it was difficult to bring experimental and theoretical results in agreement with each other.

### Dimethylperoxide, $\text{CH}_3\text{OOCH}_3$

The most relevant geometric parameter for peroxides is the dihedral angle  $\Phi(\text{XOOX})$ . For dimethylperoxide this parameter has a long and controversial history and an overview is given in Table II. The interpretation of vibrational (IR/Raman) and photoelectron spectra (PES) lead to different results; that is, a skew structure with  $\text{C}_2$  symmetry and a planar trans or essentially planar trans conformation with  $\Phi(\text{COOC}) = 180$  or  $170^\circ$ . GED and far-IR studies based on large-amplitude

models result in equilibrium values of  $\Phi_c(\text{COOC}) = 119(4)^\circ$  and  $120.0(1)^\circ$ , respectively. MM, semiempirical, and *ab initio* calculations report dihedral angles between  $96^\circ$  and  $180^\circ$ . Standard *ab initio* methods with or without inclusion of electron correlation predict a planar trans conformation that is not in agreement with the experiment. The nonstandard method (MP4 calculation with MP2 geometries) reproduces the experimental dihedral angle correctly. MP2 calculations give the correct result, if a large basis set is used.

### Trifluoroethylidynesulfur Trifluoride, $\text{CF}_3-\text{C}\equiv\text{SF}_3$

The synthesis of this interesting compound was reported by Seppelt et al. in 1984.<sup>17</sup> Because it was the first compound with a  $\text{C}\equiv\text{S}$  triple bond, it attracted the interest of experimental investigators and theoreticians, whose results are shown in Table III. The slight deviation from linearity of the  $\text{C}-\text{C}\equiv\text{S}$  chain in the crystal [ $171(2)^\circ$ ] was rationalized by packing effects. The much stronger bending of this chain derived from the GED analysis [ $155(2)^\circ$ ], however, is in qualitative disagreement with HF calculations and with chemical intuition which predict a linear coordination at the *sp*-hybridized central carbon atom. To exclude any possible mistake in the experiment, such as possible decomposition of the rather unstable compound, the synthesis and GED experiment were repeated. The purity of the sample was checked before and after the experiment. A nonrigid model with free internal rotation of the  $\text{CF}_3$  group and

**TABLE II.** Experimental (in Bold) and Theoretical Values for the COOC Dihedral Angle in Dimethylperoxide.

Method	Year	$\Phi(\text{COOC})$	Ref.
<b>IR / Raman</b>	<b>1971</b>	<b>Skew (<math>\text{C}_2</math> symmetry)</b>	<b>2</b>
<b>PES</b>	<b>1975</b>	<b>180.0</b>	<b>3</b>
CNDO / 2	1975	180.0	3
STO-2G	1976	101.7	4
MINDO / 2	1977	96.5	5
<b>PES</b>	<b>1979</b>	<b>170</b>	<b>6</b>
MINDO / 3	1980	110.7	7
GVB-CI	1982	180.0	8
HF / 4-21G*	1984	115.5	9
MM2	1984	107.0	10
<b>GED</b>	<b>1984</b>	<b>119 (4)</b>	<b>11</b>
<b>FAR-IR</b>	<b>1986</b>	<b>120.0 (1)</b>	<b>12</b>
HF / 3-21G	1988	180.0	13
HF / 6-31G*	1988	180.0	13
MP2 / 6-31G*	1988	180.0	13
CISD / 6-31G*	1988	180.0	13
MP4 / 6-31G* //	1988	121.2	13
MP2 / 6-31G*			
MP2 / 6-31G*	1995	180.0	14
MP2 / 6-31G*	1996	180.0	15
MP2 / 6-311G(2d,p)	1997	116.3	16

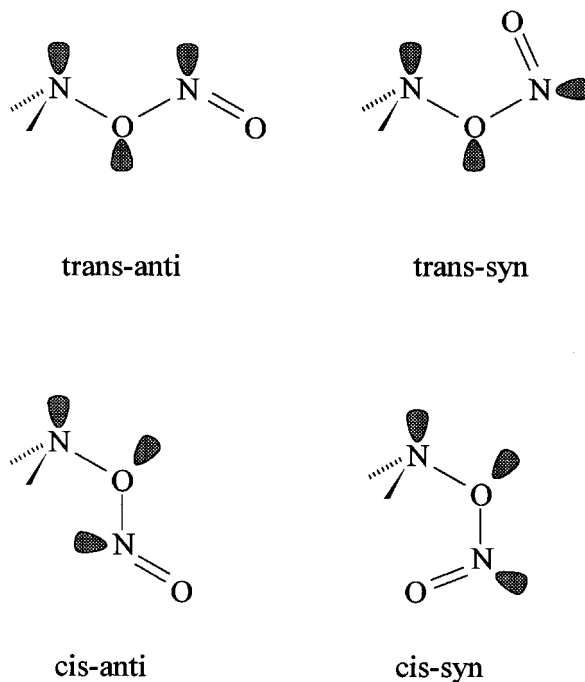
**TABLE III.** Experimental and Theoretical Results for  $\text{CF}_3-\text{C}\equiv\text{SF}_3$ .

Method	$\text{C}\equiv\text{S}$	$\text{F}-\text{S}-\text{F}$	$\text{C}-\text{C}\equiv\text{S}$
HF / 4-21G(*) (1984) <sup>18</sup>	140.4	92.7	180
X-ray, $-130^\circ\text{C}$ (1985) <sup>19</sup>	142.0 (5)	93.0 (6)	172 (2)
Preliminary GED (1985)	143.0 (15)	93.0 (11)	155 (3)
HF / 4-31G* (1986) <sup>20</sup>	141.2	92.8	180
GED (nonrigid) (1987) <sup>21</sup>	143.4 (14)	93.2 (9)	155 (2)
MP2 / 6-31G* (1987) <sup>21</sup>	141.5	92.3	148

with a large-amplitude  $C-C\equiv S$  bending motion in a double-minimum potential was used in this analysis. This experiment confirmed the previous GED result and the discrepancy with the HF calculations. Only inclusion of electron correlation effects in the MP2 approximation removes this discrepancy.<sup>21</sup>

### O-Nitrosobis(trifluoromethyl)-hydroxylamine, $(CF_3)_2NONO$

The conformational properties of this compound depend primarily on the interactions between electron lone pairs and between lone pairs and  $\sigma^*$  orbitals of vicinal bonds (anomeric effect). Assuming planarity of the NONO skeleton, four conformations are conceivable (Scheme 1). The O—N bond can be oriented trans or cis with respect to the CNC bisector and the N=O double bond can be oriented anti or syn relative to the N—O single bond. Vibrational spectroscopy and GED result in a mixture of 80(10)% trans-syn and 20(10)% trans-anti conformers.<sup>22</sup> This corresponds to  $\Delta G^0 = G^0(\text{trans-anti}) - G^0(\text{trans-syn}) = 0.8$  (3) kcal/mol. In the solid state only the trans-syn form exists. This result is unexpected, because very short contacts (252 pm in the gas phase and 248 pm in the crystal) occur between the terminal oxygen and the amino nitrogen. According to HF calculations the two cis forms do not correspond to stable structures or possess relative energies which are 5 kcal/mol above the trans forms. Standard *ab initio* methods give rather different predictions about the relative energies of the trans-syn and trans-anti conformation, ranging from  $-0.6$  to  $\pm 3.3$  kcal/mol (Table IV). This compound possesses an additional unusual property; that is, a very long O—N( $sp^2$ ) bond of 157.2(21) pm in the gas phase and 166.9(3) pm in the crystal. Our *ab initio* calculations predict this bond length between 140 and 172 pm, and none of the results is close to the experimental value.



SCHEME 1.

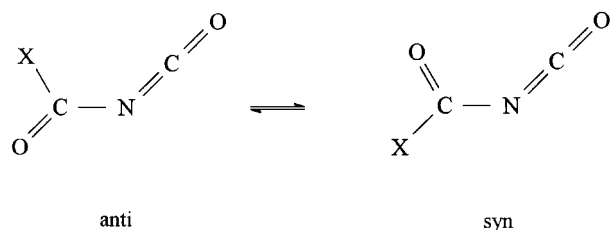
### Chlorocarbonyl Isocyanate, $ClC(O)NCO$

Compounds with 1,3-conjugated double bonds can, in general, adopt synperiplanar, antiperiplanar, or synclinal orientation of the two double bonds. In this context we studied the carbonyl isocyanates,  $XC(O)NCO$ , with  $X = CH_3, F$  and  $Cl$ . Planar anti and/or syn forms are expected for these compounds (Scheme 2). According to MW spectroscopy,<sup>23</sup> GED,<sup>24</sup> and vibrational spectroscopy,<sup>25</sup> only the syn structure is observed for acetyl isocyanate,  $CH_3C(O)NCO$ , in the gas phase. The contribution of a possible anti conformer is estimated to be less than 3%, that is,  $\Delta G^0 = G^0(\text{anti}) - G^0(\text{syn})$  is larger than 2 kcal/mol. This experimental result is reproduced correctly by *ab initio* calculations which predict  $\Delta E = 3.8$

TABLE IV.  
Relative Stabilities of Trans-Syn and Trans-anti Conformers and O—N Bond Lengths in  $(CF_3)_2NONO$  from Experiment and Theory.<sup>22</sup>

	GED	X-ray	HF/3-21G	HF/6-31G*	MP2/6-31G*
$\Delta G^0 / \Delta E^a$	0.8 (3)	—	1.8	-0.6	3.3
O—N( $sp^2$ )	157.2 (21)	166.9 (3)	152.7	140.1	171.7

<sup>a</sup> $\Delta G^0 = G^0(\text{trans-anti}) - G^0(\text{trans-syn})$  in kilocalories per mole.



SCHEME 2.

kcal/mol (HF/6-31G\*) or 2.4 kcal/mol (MP2/6-31G\*).<sup>24</sup> A GED study of fluorocarbonyl isocyanate results in a mixture of 75(12)% syn and 25(12)% anti forms. This corresponds to  $\Delta G^0 = 0.7$  (3) kcal/mol.<sup>26</sup> Theoretical calculations predict  $\Delta E$  values between 0.4 and 1.7 kcal mol<sup>-1</sup>, in good agreement with the experiment.

Chlorocarbonyl isocyanate, ClC(O)NCO, was studied by GED and vibrational spectroscopy and, with both methods, a preference of the anti conformer [75(8)% and 79(5)%, respectively] was determined for this compound.<sup>27</sup> This corresponds to  $\Delta E = -0.6$  (3) and  $-0.7$  (2) kcal/mol, respectively (the experimental  $\Delta G^0$  values were converted to  $\Delta E$ ). Various *ab initio* calculations at the HF and MP2 level, however, predict the preference of the syn form with  $\Delta E$  between 0.4 and 1.6 kcal/mol. This discrepancy challenged two other research groups which reported additional *ab initio* calculations for this molecule.<sup>28,29</sup> A selection of the ca. 40 different calculations is given in Table V. The theoretical values for  $\Delta E$  vary from  $-4.9$  (VI) to  $+7.4$  kcal/mol (VII). MP2 single-point calculations

with two sets of d functions (XI and XII) reproduce the experimental value perfectly, independent of the geometry used. Further increase of the basis set, however, makes the agreement worse ( $\Delta E = -2.5$  kcal/mol in IX). Density functional methods (XIII and XIV) lead, in this case, to perfect agreement with the experiment. This molecule demonstrates how difficult it may be to make a reliable prediction of conformational properties, even for a very small molecule.

### Tetrakis(dimethylamino)ethene, (NMe<sub>2</sub>)<sub>2</sub>C=C(NMe<sub>2</sub>)<sub>2</sub>

For this compound a structure with a nonplanar N<sub>2</sub>C=CN<sub>2</sub> skeleton, which is twisted around the C=C bond, was determined by X-ray crystallography [ $\tau(\text{C}=\text{C}) = 28.3(5)^\circ$ ] and GED [ $\tau(\text{C}=\text{C}) = 28(2)^\circ$ , C<sub>2</sub> symmetry]<sup>31</sup> (Table VI). In contrast, the isoelectronic tetraisopropylethene possesses a planar skeleton in the solid state.<sup>32</sup> On the other hand, various theoretical methods predict a strongly twisted structure for tetra-*tert*-butylethene, with  $\tau(\text{C}=\text{C}) \sim 47^\circ$ .<sup>33</sup> In the latter compound, the torsion around the double bond is caused by steric interactions between methyl groups of cis-standing *tert*-butyl substituents. No such close contacts between methyl groups occur in (NMe<sub>2</sub>)<sub>2</sub>C=C(NMe<sub>2</sub>)<sub>2</sub>. The twist around the double bond must be due to repulsion between the electron lone pairs of cis-standing dimethylamino groups. Semiempirical, MM3, and HF calculations

**TABLE V.** Selected Values for Theoretical Energy Differences  $\Delta E = E(\text{anti}) - E(\text{syn})$  (in kcal / mol<sup>-1</sup>) for ClC(O)NCO.

	Method	$\Delta E$	Ref.
(I)	HF / 4-31G(d)	+1.3	27
(II)	HF / 6-31G(d)	+1.6	27
(III)	MP2 / 4-31G(d)	+0.6	27
(IV)	MP4SDTQ / D95(d) // MP2 / 4-31G(d)	+0.4	27
(V)	MP2 / 6-31G(d)	+0.6	28
(VI)	MP4 / 6-31G(d)	-4.9	28
(VII)	HF / 6-311G(d) // MP2 / 6-31G(d)	+7.4	28
(VIII)	MP2 / 6-311G(d) // MP2 / 6-31G(d)	-1.7	28
(IX)	MP2 / 6-311 + G(2d) // MP2 / 6-31G(d)	-2.5	28
(X)	HF / 6-31G(2d) // HF / 6-31G(d)	+0.8	29
(XI)	MP2 / 6-31G(2d) // HF / 6-31G(d)	-0.7	29
(XII)	MP2 / 6-31G(2d) // MP2 / 6-31G(d)	-0.7	29
(XIII)	LDFT	-0.6	30
(XIV)	NLDFT	-0.5	30
	GED experiment	-0.6(3)	27

**TABLE VI.**  
**Experimental and Theoretical Twist Angles**  
 $\tau(\text{C}=\text{C})$  in  $(\text{NMe}_2)_2\text{C}=\text{C}(\text{NMe}_2)_2$ .

Method	$\tau(\text{C}=\text{C})$	Ref.
X-ray 1991	28.3 (5)	31
GED 1991	28 (2)	31
AM1 1991	Planar	31
MM3 1993	Planar ( $\text{C}_1$ symmetry)	34
MM3 1994	Planar ( $\text{C}_{2h}$ symmetry)	34
HF / 6-31G* 1996	2.8	35
B3PW91 / 6-31G* 1997	18.7	35

predict a planar or nearly planar skeleton. Only the DFT method reproduces the torsion around the  $\text{C}=\text{C}$  bond qualitatively, but the calculated value is ca.  $10^\circ$  smaller than the experimental result.

## Conclusion

The combination of experimental and theoretical methods for the determination of geometric structures and conformational properties of molecules is a big advantage to the experimental investigator. It leads to an increased accuracy of the experimental results. Such a combination is also advantageous for the theoretician. The selected examples demonstrate that predicted structures or conformational properties may depend strongly on the theoretical method. It is certainly possible to find a suitable theoretical approach that reproduces the experimental results in each of these cases. Without the knowledge of the experimental result, however, it is not possible to select the suited method for each molecule *a priori*. This general problem of computational chemistry was addressed by Dewar several years ago.<sup>36</sup> "Any valid use of *ab initio* procedures in chemistry has therefore to be on a purely **empirical** basis, limited to situations where specific tests have shown the procedure in question to give satisfactory results."

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